PARTITIONING OF CESIUM IN HYDROFRACTURE GROUTS*

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ABSTRACT

Phase characterization of hydrofracture grouts was accomplished with the use of optical microscopy, scanning electron microscopy, x-ray diffraction, and β - γ autoradiography. A laboratory-produced sample containing 1 wt % stable cesium and an actual hydrofracture grout sheet obtained by core drilling were examined during this work. The phases present in these samples were identified and cesium was found to be absorbed almost entirely by illite clay agglomerates. These clay agglomerates were tightly bound within the grout structure by hydrated calcium silicates. The β - γ autoradiography of the core-drilled sample verified that cesium and other radionuclides were trapped within the 20-year-old grout and had not migrated into trapped shale fragments.

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INTRODUCTION

The hydrofracture process permanently disposes of solidified low-level radioactive liquids and sludges generated at the Oak Ridge National Laboratory (ORNL)[1,2]. This process immobilizes and isolates the radioactive liquid and sludge waste in a cementitious grout by injecting the grout into an impermeable shale formation 200-300 meters below the earth's surface. The disposal cost of liquid waste by this process is from \$0.40-0.50/liter (\$1.50-2.00/g). These costs are significantly lower than other methods of disposal, such as borosilicate glass, Synroc, tailored ceramics, coated sol-gel-derived ceramics, or concrete [3-7].

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The hydrofracture facility has been used since 1966 for the disposal of low-level wastes generated at Oak Ridge National Laboratory. The low level waste is composed of a mixture of all the liquid wastes produced in hot-cell, pilot plant, and reactor operations. The solution after concentration by evaporation may contain up to 2 Ci of beta-gamma activity per gallon. The major radionuclide present is generally ^{137}Cs while ^{90}Sr is present at a level of 0.1 Ci/gal or less. The major alpha activity is ^{244}Cm with a maximum concentration of 1 m Ci/gal. The liquid waste is blended with cement and other additives and immediately pumped at about 700 liter/min (150–200 gal/min) into the fractured shale creating a thin horizontal sheet several hundred meters in diameter. The well remains pressurized for several days while the grout hardens. Numerous injections can be made into each fracture; and fractures are spaced 2 to 4 meters apart between the 200- and 300-meter level of the well. The hydrofracture facility consists of a series of shielded cells housing the associated pumps, mixers, piping and the actual well head, as well as large, external, solids storage tanks, and a liquid-waste tank farm (Fig. 1).

The shale-fracturing process assures the fixation of radionuclides in a geologic formation known to be isolated from contact with the surface environment or with subsurface aquifers. The permeability of shale in the ORNL disposal zone is very low, therefore ensuring minimal water movement. The process had additional features which provide continued containment of radionuclides even if the isolation of the disposal formation were lost. The leach rates of significant radionuclides from the set grout are approximately equal to those of borosilicate glass [8,9]. In addition, only radionuclides that might be leached from the grout sheet would be retained in the disposal zone by the high ion exchange

capacity of the shale. Therefore, this process offers an inexpensive but very effective approach for the permanent disposal of radioactive wastes.

Our objective in this work was to identify the various phases present in hydrofracture grouts, and determine the partitioning of cesium into these phases. A second objective was to verify that radio-nuclides are fixed within these phases and do not migrate into the surrounding shale.

EXPERIMENTAL PROCEDURE

Phase characterization studies of hydrofracture grout samples were conducted on typical grout compositions containing 1 wt % cesium. This grout consisted of cement, fly ash, [10,11] illite clay, and attapulgite clay in the proportions shown in Table I. Fly ash is added to grout compositions as a partial substitute for cement to reduce the cost and

TABLE I

Composition of hydrofracture grouts

Constituent	Composition (wt %)	
	Dry solids blend	Final grout
Portland cement	38	15
Fly ash	38	16
Illite clay	8	4
Attapulgite clay	16	8
Cesium		1
Water		55

to improve the retention of strontium. Attapulgite is a drilling clay that suspends the cement and absorbs water, thereby reducing the phase separation. Illite clay is added for its high capacity for cesium retention. Samples of grout containing 1 wt % stable cesium were prepared and allowed to hydrate for one month. Hydration was stopped at this point because the high porosity present would make examination by scanning electron microscopy much easier. Samples previously examined were several years old and therefore very dense and difficult to analyze.

A second sample obtained from a core drilling of an actual hydrofracture grout sheet injected in 1964 was also examined. This sample containing ^{90}Sr , ^{137}Cs , and ^{60}Co was cured in situ for two years and cored and stored above ground since 1966 [12]. The composition of the dry solids used for this injection was 86% cement, 8% attapulgite clay, and 6% illite clay. This was an early composition that did not contain fly ash and had not been optimized to minimize leachability.

The techniques used for the examination of grout samples were x-ray diffraction, optical microscopy, scanning electron microscopy combined with energy dispersive x-ray analysis, and autoradiography. Samples examined by scanning electron microscopy were polished sections or fresh fracture surfaces.

RESULTS AND DISCUSSION

Hydrofracture grouts are composed primarily of cementitious phases produced from the hydration of portland cement. However, the phases present in actual grouts are more complex because of the addition of fly ash, and various clays, and the interaction of the wastes with the cementitious phases. The phases normally present in hydrated cement are

calcium silicate hydrate, calcium hydroxide, ettringite, and a hydrated calcium aluminoferrite [13,14]. Typical hydrofracture grouts examined after several years hydration were found by x-ray diffraction to consist primarily of calcium carbonate phases. Calcite (CaCO_3) was the predominant phase, with vaterite (another crystal structure of CaCO_3) also present. Apparently Ca(OH)_2 formed during hydration of portland cement reacted with air to form carbonates. Other phases identified in these samples were quartz (SiO_2), mullite ($3\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), a magnetitelike spinel (Fe_3O_4), attapulgite clay, and unhydrated dicalcium silicate. The quartz, mullite and magnetitelike spinel were from unreacted fly ash particles.

Examination by scanning electron microscopy permitted the identification of phases detected by x-ray diffraction. Fly ash particles could be easily identified because of their spherical morphology (Fig. 2). Their elemental composition of silicon, aluminum, and iron was consistent with the phases of quartz, mullite, and magnetite identified by x-ray diffraction. Large crystalline areas of calcium hydroxide appeared throughout the microstructure. After only one month of hydration calcium hydroxide had not yet reacted with CO_2 from the air to form CaCO_3 . The calcium hydroxide had the characteristic appearance of a stack of flat lamella. All features present in the microstructure appeared to be bonded together with calcium silicate hydrate.

The sample was examined with the elemental dispersive x-ray analysis system in order to locate the 1 wt % cesium that had been added. The cesium was almost entirely absorbed by the illite clay, which appeared as large agglomerates dispersed throughout the microstructure. These agglomerates were bound into the structure by the hydrated calcium silicate. No detectable amounts of cesium could be found in the calcium hydroxide or the hydrated calcium silicate phases.

The core-drilled sample of grout was examined by optical microscopy, scanning electron microscopy, and x-ray diffraction and was found to consist of the same phases as grout produced in mix development studies. Examination by scanning electron microscopy failed to reveal the strontium, cesium, or cobalt because of the very low concentrations. The sensitivity of the energy-dispersive system is about 0.1%; the samples must therefore contain less than 0.1% strontium, cesium, and cobalt. Examination by ion microprobe and transmission electron microscopy also failed to reveal the radionuclides. However, the radionuclides were located by β - γ autoradiography (Fig. 3a). The sample was placed on film that was sensitive to β - γ radiation and left for three days; the exposure was required because of the very small amount of activity present. Numerous fragments of shale were trapped in the grout as it was forced into the fracture. The dark areas of the bright-field photograph are shale fragments, and the light areas are grout. The light areas in the autoradiograph correspond to areas of strontium, cesium, or cobalt concentrations. The autoradiograph clearly shows that the activity has remained in the grout and has not migrated into the shale after nearly 20 years. Although the grout was cured in situ for only two years, the shale fragments were trapped within the grout for the full 20 years.

CONCLUSIONS

The phases present in hydrofracture grouts were identified by various methods to be calcium carbonate or calcium hydroxide in samples hydrated only one month, quartz, mullite, magnetite-like spinel, unhydrated dicalcium silicate, attapulgite clay, and illite clay. The cesium added to the grout was absorbed almost entirely by the illite clay.

This result has been suspected for some time but never verified. There were no detectable amounts of cesium associated with the other phases. Apparently, the grout stabilized cesium by sorbing it onto the illite clay and trapping the illite clay agglomerates within the cementitious structure.

Radionuclides in a core-drilled sample were present in extremely small quantities and could not be detected by scanning electron microscopy or other microscopic techniques. However, a β - γ autoradiograph clearly showed that radionuclides were fixed within the grout and did not migrate into the shale in 20 years. These results provide convincing evidence that disposal of radioactive wastes by hydrofracture is an effective means of waste disposal.

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Fig. 1. Oak Ridge National Laboratory hydrofracture facility.

Fig. 1. Oak Ridge National Laboratory Grouted Waste Injection Facility.

looks like Polaroid

Fig. 2. Scanning electron micrograph of hydrofracture grout
hydrated one month.

Fig. 2. Scanning Electron Micrograph of Grout
Hydrated One Month.

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Fig. 3. Cored grout shows no migration of radionuclides in beta-gamma autoradiograph (left). Dark areas in the bright-field photograph (right) are shale fragments. Corresponding areas in the autoradiograph contain neither ^{90}Sr , ^{137}Cs , nor ^{60}Co activity.

Fig. 3. Cored Grout Shows No Migration of Radionuclides in β - γ autoradiography (left). Dark areas in the bright-field photograph (right) are shale fragments. Corresponding areas in the autoradiograph contain neither ^{95}Sr , ^{137}Cs , nor ^{60}Co activity.